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Structure Determination of Framework-doped Tunnel Structure Manganese Oxides Using EXAFS and XANE

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Introduction: Framework doped tunnel structure octahedral molecular sieves (OMS) have exceptional catalytic properties due to the mixed valent Mn and the selective doping of metals. EXAFS and XANES can be used to obtain information such as the spatial relationships of metal atoms and surrounding atoms, oxidation states of metal atoms, and the identification of possible amorphous metal oxides, which cannot be readily obtained by other techniques.

Methods and Materials: Transition metal cations were first doped into the MnO_6 octahedron layers of layered structure birnessite, which served as a synthetic precursor for tunnel structure cryptomelane. Transition metal-doped cryptomelane was then obtained by the thermal transformation of metal-doped birnessite. Cryptomelane samples were grounded into fine powders and calculated amounts of samples (10 –20 mg) were weighed for different metal doped cryptomelane. Cryptomelane was put on scotch tapes and distributed evenly to ensure homogeneity. In each sample, the signals of Mn and the doped transition metals were recorded.

Results: The EXAFS signals of Mn and doped transition metals showed transition metals were doped into tunnel structure manganese octahedral molecular sieve cryptomelane under certain doping limit using our framework doping method. Doping limits for different transition metals were observed for cryptomelane samples. The shifts of the doped transition metal signals in excessively doped samples showed changes in the local chemical environments. Doped iron was found to be in framework sites in synthetic cryptomelane under doping limit.

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